Chapter

Stress Corrosion Cracking Behavior of Materials

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Abstract

Stress corrosion cracking is a phenomenon associated with a combination of tensile stress, corrosive environment and, in some cases, a metallurgical condition that causes the component to premature failures. The fractures are often sudden and catastrophic, which may occur after a short period of design life and a stress level much lower than the yield stress. It can also occur after several years of satisfactory services due to operating errors and changing process conditions. Two classic cases of stress corrosion cracking are seasonal cracking of brass in ammoniacal environment and sensitization and stress corrosion cracking of stainless steels in existence of chlorides, caustic, and polythionic acid. Presence of crack and other defects on the material surfaces accelerates the fracture processes. Therefore, when designing components, the role of imperfections and aggressive agents together must be taken into account. The fracture mechanic introduces a material characteristic namely fracture toughness or $K_{ISCC} = \sigma\sqrt{\pi a}$, which properly describes the fracture behavior of materials in such conditions. The main objective in writing of this chapter is to present scientific findings and relevant engineering practice involving this phenomenon.

Keywords: stress corrosion cracking, fracture mechanic, mechanism

1. Introduction

Stress corrosion cracking (SCC) is service failure of engineering materials that occurs by slow, environmentally induced crack propagation. Identification of SCC occurred between 1930s and 1950s, the mechanism of SCC was explained between 1960s and 1970s and its application and development began at 1980s [1]. In fact, the industry owners did not find the austerity of the problems connected to the stress corrosion cracking until the tragic rupture of a digester at Pine Hill, Alabama, in 1980 [2]. After the accident, considerable investigations have been taken on SCC phenomenon. In this type of failure, the crack commencement and growth is the consequence of reciprocal action of sensitizes material, tensile stress, and corrosive environment.

Various types of SCC have been distinguished. Chloride SCC appears in austenitic stainless steels under tensile mechanical stress in the existence of chloride ion, oxygen, and a high temperature condition [3]. Cracking of stainless steels under caustic environments in the presence of a high hydrogen concentration is known as caustic embrittlement [4]. SCC cracking of steels in hydrogen sulfide environment is confronted in oil industries [3]. Cracking of brass in ammonia environments is another type of SCC, which is known as sessional cracking.

During SCC phenomenon, the material is essentially unattacked over most of its surface, while fine and branch cracks develop into the bulk of material [5]. This cracking phenomenon has serious consequences since it can occur under stress levels much lower than the designer intended and cause the equipment and structural elements to catastrophic fractures [6–10].

In this chapter, the feature of SCC is first introduced. Then, the requirements of the stress corrosion cracking are expressed. In next step, the mechanisms attributed to this corrosion phenomenon are discussed in detail. Designing of structural elements and mechanical equipment based on the tensile properties may be led to false results. Accordingly, the science of fracture mechanics applies in situation where SCC can be occurred. Fracture mechanic presented criteria that considered the role of imperfection on the fracture of materials. Next, based on the corrosion science and empirical data, the methods of preventions are presented. Finally, case studies are introduced to better understand of the issue.

2. SCC features

In macroscopic scale, SCC failures appear to be brittle even if the material is ductile, and stress level is lower than design stress. The cracks in SCC are not mechanical but are caused by corrosion. A typical growth and developments of cracking by cause of the stress corrosion cracking phenomenon in AISI316L stainless steel are shown in **Figure 1a**.

The branches developed, intergranular and transgranular cracks are the character of stress corrosion cracking in microscopic levels, **Figure 1b**. In intergranular mode, the cracks proceed along grain boundaries while transgranular cracks grow across the grains [3]. The mode of crack proceeds depends on the material microstructure and environment.

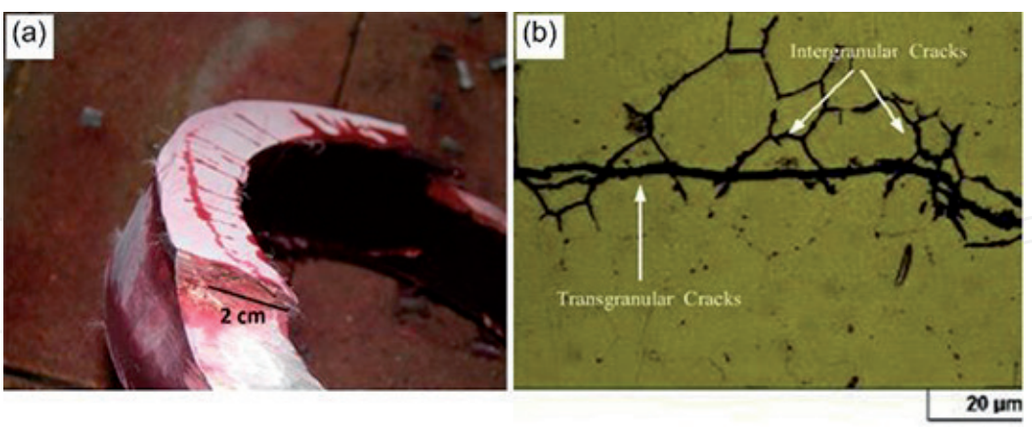

Figure 1.
Macroscopic and microscopic feature of the stress corrosion cracking: (a) Cross-section of a failed tube and formation of macro branching cracks on it. (b) Optical micrograph of a typical SCC in AISI316L stainless steel exposed to chlorides [3, 4].

3. Requirement for SCC

Three key elements are essential for initiation and growth of the stress corrosion cracking: a sensitized material, a specific environment, and adequate tensile stress. It is shown in **Figure 2**.

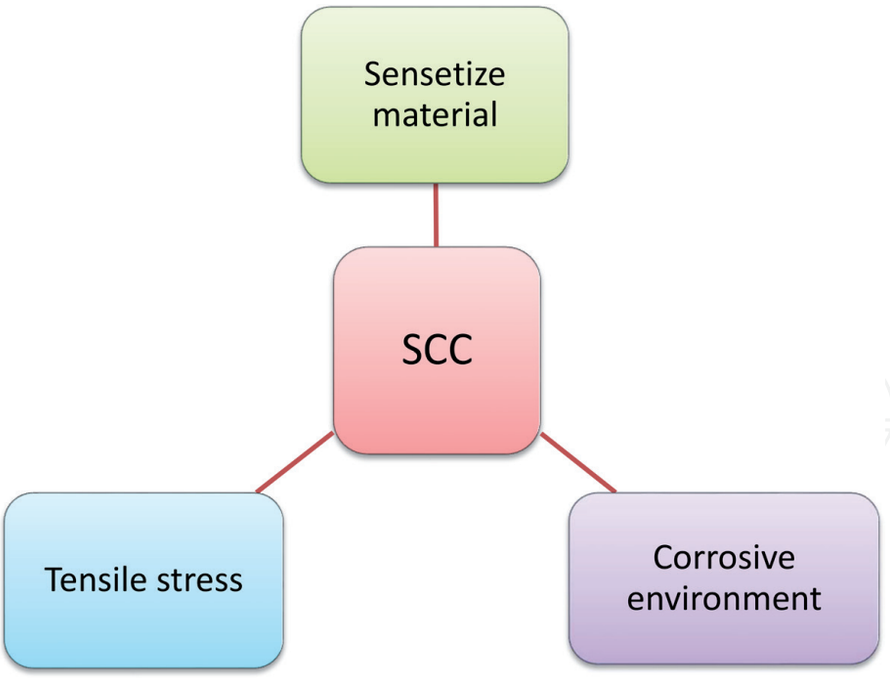

Figure 2.
Essential parameters for occurring SCC.

3.1 Materials

3.1.1 Stainless steels

When austenitic stainless steel grades contain more than 0.03 wt% that are exposed to temperature from 415 to 850°C, their microstructure becomes sentient to precipitation of chromium carbides ($M_{23}C$) along grain boundaries called as sensitization [11, 12]. Constitution of Cr enrichment carbides along with grain boundaries may severely evacuate the area aside to the grain boundaries from free chromium and render them sensitive to rapid corrosion in presence of aggressive agents such as chloride, caustic, and polythionic acid [4, 12, 13]. Grain boundary dissolution aside tensile tress lead the component made of these ductile alloys to brittle fracture. An example of the SCC failure in an austenitic stainless steel is shown in **Figure 1**.

3.1.2 Copper and copper alloys

Copper is alloyed with zinc, tin, nickel, aluminum, and silicon to produce various types of brass, bronze, cupronickel, aluminum bronze, and silicon bronze, respectively. Most of SCC failure mechanisms for copper-based alloys have been predominantly investigated for ammonia-brass systems [14]. A classic example of SCC for brass systems is season cracking. It specifies the stress corrosion cracking of brass cartridge cases of British forces in India [11]. Two mechanism have been found to be attributed to SCC of copper-based alloys: (a) the passive film rupture and (b) de-alloying [15]. According to first theory, intergranular SCC is to occur due to passive-film rupture and transient dissolution mechanism in copper-zinc alloys. Chen et al. reported that aluminum bronze (Al-Cu-Zn) underwent SCC in fluoride-containing solutions through the film-rupture mechanism [16]. According to de-alloying, that is, selective segregation of the alloying elements, for example, Zn in Cu-Zn systems, is the primary factor in the stress corrosion cracking phenomenon. For example, in the case of Cu-Zn alloy systems, preferential segregation of Zn take place in the crack

tip region, or along the grain boundaries. Domiaty and Alhajji found that cupronickel alloy Cu-Ni (90–10) underwent SCC in seawater polluted with sulfide ions due to selective dissolution of copper [17]. Chen et al. also reported that de-alloying resulted in SCC of aluminum brass (Al-Cu-Zn) in fluoride-containing aqueous solutions [16]. The Pourbaix diagrams for pure metals can be helpful in anticipating the sensitivity to de-alloying and in appraising the tendency of selective dissolution and hence the SCC behavior [16].

3.1.3 Carbon steels

Stress corrosion cracking of carbon steels has been identified as one of the main reasons leading to leakage and rupture events of pipe lines and steam generator boilers with catastrophic consequences [18, 19]. Carbon steels have shown SCC in conditions that there is a desire to form a protective passive layer or oxide film [13, 20–22]. In fact, the environments where carbon steel is susceptible to SCC are carbonates, strong caustic solutions, nitrates, phosphates, and high-temperature water [13, 23–25]. The problems associated with SCC in carbon steels are influential for both economic and safety reasons, because of widespread use of these alloys in various industries.

3.1.4 Aluminum and aluminum alloys

Aluminum and its alloys are extensively used in military, aerospace, and structural applications. These groups of engineering material under specific environment and sufficient magnitude of stress are susceptible to SCC [26, 27]. Determinant factor on the stress corrosion cracking behavior in Al alloy systems is the chemical composition. Alloying elements have strong influences on the formation and stability of the protecting layer on the surface of alloy and also may show effects on the strength, grain size, grain boundary precipitations, and magnitude of residual stress within the material [28, 29]. In between them, series of 2xxx, 7xxx, and 5xxx (alloys containing magnesium) are sensitive to SCC [28]. Failures associated with SCC in aircraft constituents made of 7075-T6, 7079-T6, and 2024-T3 Al-alloys were reported between 1960 and 1970 [27].

Another important factor on SCC behavior of aluminum alloys is type of heat treatment and quenching rates [26, 30]. Heat treatment shows a crucial role in formation and organization of the constituent particles in order to attain a high strength aluminum alloys. It has been reported that aluminum alloy series 7xxx are sensitive to cooling rate and many researchers investigated the effect of cooling rates on the stress corrosion cracking behavior of the alloys. Researches have displayed that a decline in the cooling rate results in a rise in the size and inter particle distance of the GBP forward with an increase in width of the PFZ. Unfortunately, this leads to a decrease of copper contents in the grain boundary of precipitates and reduction of resistance to SCC [28–30].

There is a significant discrepancy in the texts on the exact mechanism of stress corrosion cracking in Al alloys. Evidence shows that the proposed mechanism of SCC pertains on the alloy system in question: anodic dissolution is suggested for the 2xxx alloy systems (AI-Cu and Al-Cu-Li), while hydrogen-induced cracking or HIC is presented by most investigators in the 5xxx and 7xxx alloys. Another mechanism may be properly explained SCC in some Al alloy systems is the rupture passive film. Thus, while SCC phenomenon of Al alloys is well documented, the actual mechanisms are still challenged [29].

Two methods are suggested improving SCC resistance in Al alloys. The first method is to break down the continuity of the GBPs and the second is to decline the galvanic potential nonconformity between the grain boundaries and matrix.

3.1.5 Titanium and titanium alloys

Titanium alloys are broadly utilized in aerospace industry because of their high corrosion resistance and specific strength. Two widely used grades of Ti are Ti-6Al-4 V known as Ti-64 alloy and Ti-8Al-1Mo1V known as Ti-811. The latter is specified by its lower density and surpassing stiffness, but unfortunately is susceptible to SCC.

The significant corrosion resistance of Ti alloys under oxidizing media is a result of formation of the protective passive TiO_2 film on the surface. For Ti-811 grade, instinctive passivation arises in 3.5% sodium chloride HCl solution [31]. However, the passive protective layer will be destroyed if load applied is over the yield stress of the oxide film, and corrosive environment will then expose to the fresh metal and lead to SCC [32]. In Ti alloys systems, oxygen and aluminum additions enhance SCC sensitivity and change the slip condition to a planar slip [33]. Slip plan growth of SCC cracks in this grade of Ti alloys is shown in **Figure 3**.

3.1.6 Polymers

SCC can be occurred in polymers, when the components made of these materials are exposed to specific aggressive agents like acids and alkalis. Similar to metals combination of polymer and environment which lead to SCC is specific. For instance, polycarbonate is susceptible to SCC in alkalis, but not by acids. On the other hand, polyesters are prone to SCC when exposed to acids [34]. Another form of SCC in polymeric materials is ozone attack [35]. Small traces of the gas in the air will attack polymer bonds and lead them to degradation. Natural rubber, nitrile butadiene rubber, and styrene-butadiene rubber were found to be most sensitive to this form of failure. Ozone cracks are very dangerous in fuel pipes because the cracks can grow from external surfaces into the bore of the pipe, and so fuel leakage and fire will be its consequences [36–38]. Investigations have shown a critical amount of deformation and ozone concentration require for SCC crack growth in rubbers [35].

3.1.7 Ceramics

The stress corrosion cracking is less common in ceramic materials that are more resistant to chemical attacks. However, phase transformation under stress is usual in the ceramic substances such as zirconium dioxide. This phenomenon led them to toughening [39]. Silica or SiO_2 is extensively used in microelectromechanical

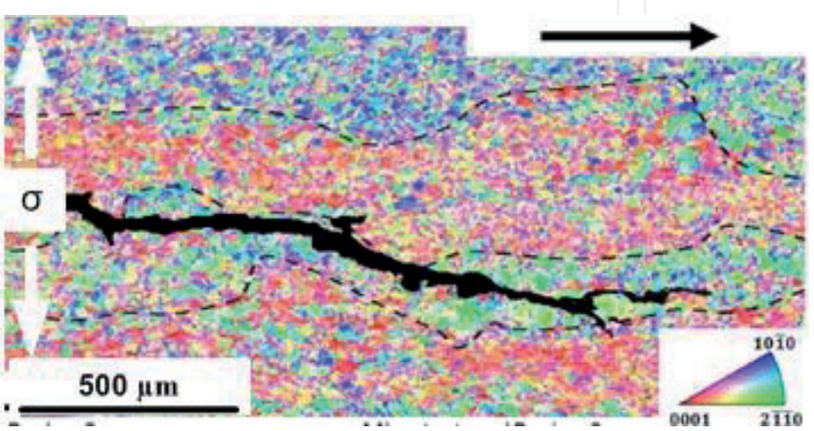

Figure 3.
IPF map of the SCC crack growth in a wrought Ti-811 specimen. Crack propagation extended along planar slip (0001) [33].

systems and in integrated circuits as sacrificial release layers and dielectric layers. Silica is sensitive to SCC in air because of the reaction between Si-O bonds with H_2O molecules under stress [40].

3.2 Environments

The environment prone to stress corrosion cracking is special since not all environments provide condition for cracking. The corrosive condition may be a permanent service environment, such as processes water for a heat exchanger, or temporary environments produced by an operational errors, like deposits form on the equipment during shut downs in chemical plants. Moreover, environments that lead the components to SCC are often aqueous in nature and can be either a thin layer of condensed moisture or a volume solution [41]. Generally, the stress corrosion cracking occurs in aqueous medium, but it also occurs in certain metals, fused salts, and inorganic liquids [11]. The aggressive environment to passive film of stainless steels is chlorides, caustic, and polythionic acid. The austenitic stainless steel series 300 like AISI304 and AISI316 are more sensitive in environment consisting of chlorides. It was reported that the SCC in austenitic stainless steels containing chlorides proceeds transgranulary and often develops at a temperature over 70°C [42, 43]. Caustic embrittlement or the SCC induced by caustic is another severe problem in the equipment made of austenitic stainless steels and led to many explosions in the steam boilers and super heaters [4, 44, 45]. It was also seen that the existence of sulfur in feed gas in petrochemical plants causes forming of polythionic acid (H_2SxO, x = 2 to 5), which in presence of moisture also induced intergranular SCC in austenitic stainless steels [46, 47].

Carbon steels are found to be sensitive to SCC in nitrate, NaOH, acidic H_2S, and seawater solutions [48]. Soil environment is responsible for SCC cracking of underground pipeline carbon steels where cathodic protection is utilized to preserve lines against general corrosion [49, 50]. Cathodic protection of buried pipelines can result in the production of alkali solutions at the pipe surface where the coating is disbanded. The formed alkalis consist of sodium hydroxide, carbonate, and bicarbonate solution. Investigations have shown that in the presence of these compounds and some range of potential protection carbon steel pipes fail due to the stress corrosion cracking. For instance, carbonate solution and a corrosion potential [between −0.31 and −0.46 V (SHE)] developed the stress corrosion cracking in a high strength carbon steel pipeline [49, 50].

Environment conditions that lead the copper alloys to SCC are ammonia, amines, and water vapor [48]. The source of ammonia may be from decomposition of organic materials [11]. In ammonia production plans, ammonia comes from leakage of the equipment and piping systems, when these components are not completely leak-proof.

In aluminum and aluminum alloy, pure aluminum is safe to SCC. On the other hand, duralumin alloy refers to aluminum-copper alloys, under tension stress aside of moisture, and it may fail due to cracking along the grain boundaries. Aluminum alloys are also susceptible in SCC in NaCl solution [50].

The stress corrosion cracking of pure titanium was observed by Kiefer and Harple in red fuming nitric acid for the first time [51]. Titanium alloys are also susceptible to SCC when is exposed to sea water and methanol-HCl [52].

3.3 Stress

The stresses that cause SCC are directly applied stress, thermal operational stress, residual stress or combination of all [3]. The operational stress consists of

operational applied stress and thermal stress. The operational applied stress is considered by designers and usually calculated less than the yield strength. The thermal stress is generated due to thermal cooling and heating of component during services and shut downs. The thermal stress is calculated from thermal strains that are expressed by a temperature-dependent differential expansion coefficient [13]:

$$\{\Delta\varepsilon^{th}\} = [\alpha] \cdot \Delta T \quad (1)$$

in which, $\Delta\varepsilon^{th}$ is the variation of strain, α is the thermal expansion coefficient of material, and ΔT is the changing in temperature.

The main source of stress attributed to stress corrosion cracking comes from the residual stress. The well-known sources of the residual stress are welding and fabrication processes. Residual stress due to welding plays an imperative role in the stress corrosion cracking of metal alloys. In this area, two factors are determined. First, the welding residual stress by the cause of nonuniform temperature changes during welding, which can be computed by Eq. (1). Second, in some of the steel

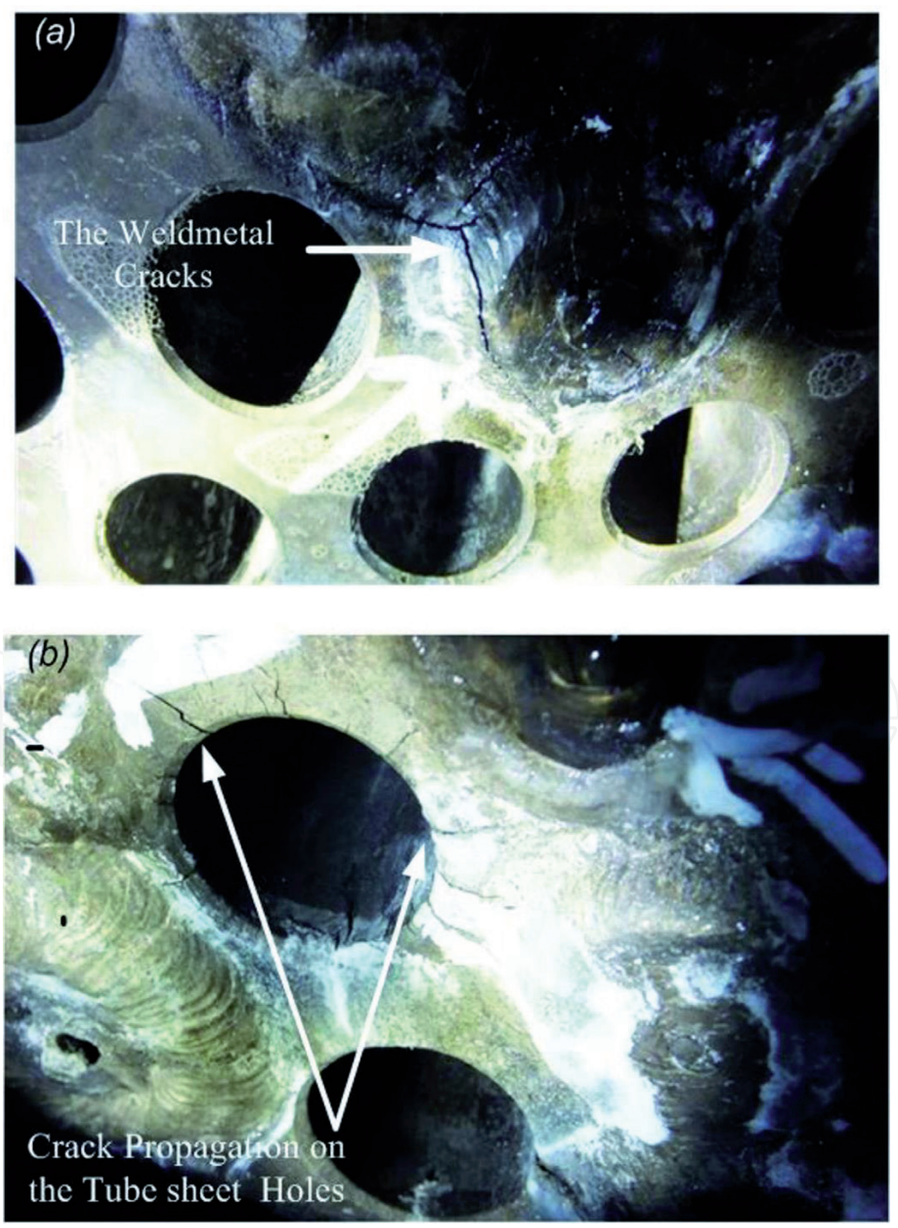

Figure 4.
Two sources of stress in the SCC: (a) welding residual stress and (b) mechanical residual stress [3].

grades, the solid-state austenite to martensite transformation in the time of cooling generates a significant value of the residual stresses [53]. In carbon and low alloy steels, martensite is formed by quenching of the austenite containing carbon atoms at such a fast cooling rate that carbon atoms do not have a chance to diffuse out from the crystal structure and form cementite. The trapped carbon atoms in octahedral interstitial sites of iron atoms, generating a body-centered tetragonal (bct) structure that is in super saturation, relate to the ferrite with body-centered cubic (bcc) structure [54]. Therefore, during this phase transformation, the volume of metal increases, and a significant residual stress is also produced [54]. In austenitic stainless steel, there are no phase transformation processes, and so this mechanism does not attribute in their welding residual stress. An example of SCC in the weld area of an austenitic stainless steel component is shown in **Figure 4a**.

The product manufacturing systems that generate considerable residual stresses include casting, rolling, forging, drilling, machining, heat treatments, cooling, carburization, and straightening [55]. In many of the material manufacturing processing, there is a rebalancing of the generated residual stresses during or after the production process, and the extent of the final residual stresses is often less than half of the yield stress or σ_y. Some material processing, such as heat treatment with slow cooling rate, may release the stresses generated by previous treatments. But processes like rapid quenching or machining, which create localized yielding at the surface, may leave residual stress in magnitude of the yield stresses at surface or down surface of the material [55]. A typical SCC in heavy machining area of an austenitic stainless steel component is presented in **Figure 4b**.

Finally, the stress must be tensile form, and comprehensive stresses do not cause the equipment to failure due to SCC.

4. Stress corrosion cracking mechanisms

The mechanism of SCC depends on the type of material and environment. Many models have been presented describing SCC phenomenon. Each of these models has its own restraints in that it can be utilized to describe SCC in limited number of metal-environment systems. In fact, there is no unified mechanism attributed in SCC for all metal environment combination. A few presented models are given in following.

4.1 Mechano-electrochemical model

According to this model, there are pre-existing regions in an alloy microstructure that become sensitive to anodic dissolution. For instance, a precipitate in grain boundary may be anodic with respect to the grain boundary and provide an active path for localized corrosion. In the same way, if a nobler phase is precipitated at grain boundaries, adjacent to precipitates provide an active track for localized corrosion. A classic example of this mechanism can be seen in austenitic stainless in which precipitates of chromium carbides along grain boundaries depletes adjacent areas from chromium and provides a path for localized corrosion to be occurred [1].

4.2 Film rupture model

The film rupture mechanism implies for the alloys which passive layer is formed on their surface. In this mechanism, plastic deformation plays the main role. The plastic strain causes film disruption on the surface of metal. After the film disruption, the bare metal is disclosed to environment, and a localized attack at the area of disruption occurs. The processes of disruption strain and film formation are

repeated, and cracking growth continues. This mechanism was originally considered for caustic cracking of boilers. It has also been utilized for description of SCC of alpha brass in ammonia environments [1].

4.3 Adsorption phenomenon

The adsorbing model is based on the process of embrittles of the material in the vicinity of a corroding area. First, the model was used to study on failure of high strength martensitic stainless steels in chloride media. According to this model, the adsorption of environmental agents drops the interatomic bond strength and the stress need for a brittle fracture. The fracture mechanic theory properly explains the issue. According to this theory, the theoretical fracture stress required to take apart two layers of inter atomics spacing b is given by:

$$\sigma_{Fr} = \left(\frac{E\gamma}{b}\right)^{1/2} \tag{2}$$

in which, E, γ, and b are Young's modulus, surface energy, and spacing between atom layers, respectively. According to this model, in corroded environments, the aggressive agents are adsorbed at the crack tip, surface energy effectively decreased, and fracture take place in a stress level much lower than the normal condition [1].

5. Application of fracture mechanic

Investigation has shown that the maximum operational stresses and the maximum defect sizes imparted during production processing could limit the life time of materials [56]. Stress produced due applied, thermal or residual, usually below the yield strength of a material. However, surface defects that either preexist or are produced during services by cause of corrosion, wear, or other processes (**Figure 5**) may provide stress concentration and so condition for fracture [41]. Hence, the role of imperfections should take into account. Fracture mechanic introduced another

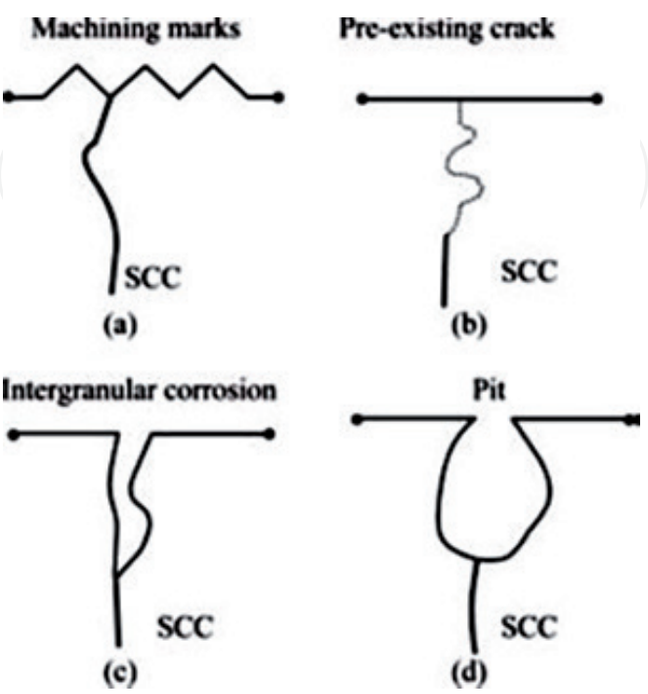

Figure 5.
The sources of SCC sites (a) machining marks, (b) pre-existing crack, (c) intergranular corrosion, and (d) pit [28].

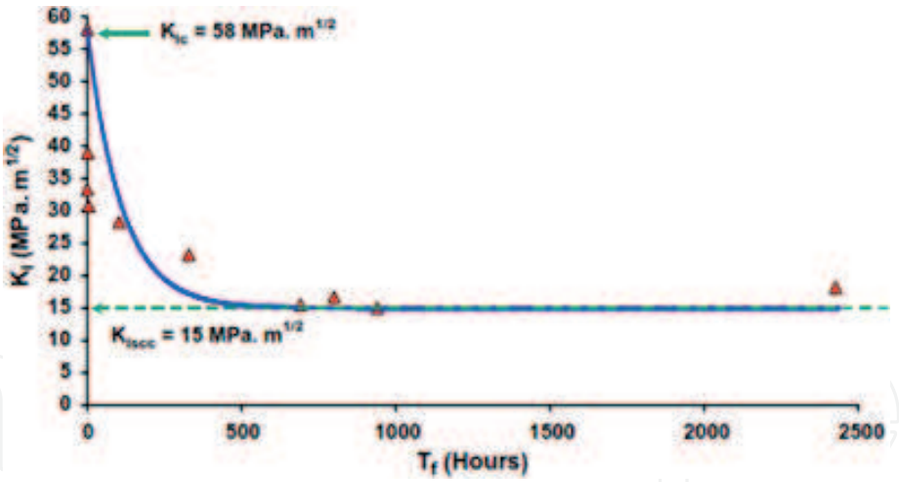

Figure 6.
K_I vs. T_f of AISI4340 steel in 3.5% NaCl at ambient temperature [59].

material property named fracture toughness or K_{Ic} in the same sense that the yield strength. The fracture toughness is a material property that expresses the resistance to crack growth. The relation between fracture toughness, flaw size, and stress in simplest form is expressed as [57]:

$$K_{Ic} = \sigma\sqrt{\pi a} \tag{3}$$

in which, σ denotes stress and a denotes crack length.

According to this relation, there is a critical size of flaw which led a component to brittle fracture. Investigation has shown that for the structure expose to corrosive environments, the scenario is quite different [58]. The corrosive environments cause a significant drop in this property of the materials [59]. This typically is shown in **Figure 6**. As it is seen from the graph, the K_{Ic} in presence of aggressive agents shown by K_{Iscc} is much lower than its value in normal conditions. This means in corrosive environments prone to SCC, a smaller flaw size led the components to catastrophic brittle fractures. Susceptibility of existing cracks to environmentally assisted propagation is a critical consideration for designers while selecting proper materials for environments prone to this form of corrosion [58].

Example 1. Compare the critical crack length for 4340 steel exposed to dry environment and 3.5% NaCl at room temperature:

If we assume that the applied load is on the magnitude of yield stress (Y.S), the critical crack depth, a_{cr}, exists above a size that the stress intensity factor exceeds K_{Ic} or K_{Iscc}. In presence of this condition, the failure occurs in a brittle mode. Based on Eq. (3):

In dry condition: $a_{cr} = \left(\frac{K_{Ic}}{Y.S}\right)^2 = \left(\frac{58}{68}\right)^2 = 0.73$ in.

In 3.5% NaCl condition: $a_{cr} = \left(\frac{15}{68}\right)^2 = 0.05$ in

The results show that the a_{cr} in presence of corrosive agents is about 15 times lower than the normal condition.

6. Prevention

Since the mechanism of SCC is not fully understood, methods of preventing are based on empirical experiences. One or more application of the following methods can be worked out in reduction or prevention of the SCC [11]:

a. Lowering the stress levels. This may be done by annealing treatment in the case of residual stress. Stress relief temperature for plain carbon steels are at a range of 1100–1200°F and for austenitic stainless steels are frequently at temperatures ranging from 1500 to 1700°F.

b. Eliminating aggressive species in the environment. For instance, in case of austenitic stainless steels, reduction of chloride under 10 ppm reduces significantly the probability of the stress corrosion cracking to occur [44].

c. Changing the material in one plane if neither environment condition nor stress level can be changed. For example, in case of AISI304, stainless steel utilizing a high nickel alloy content (e.g., Inconel) can be useful.

d. Applying cathodic protection by impressed current or sacrificial anode. In cathodic protection, note that the failure is due to SCC, not hydrogen embrittlement. In cathodic protection, the released hydrogen due to cathodic reaction can accelerate the hydrogen embrittlement.

e. Adding inhibitors such as phosphate and other organic and inorganic to the system can reduce the stress corrosion cracking effects in mildly corrosive media.

f. Coating is sometimes effective.

g. Shot-peening generates residual compressive stress in surface of the component and prevent the stress corrosion cracking to be occurred.

h. The problem associated with ozone stress cracking can be prevented utilizing anti-ozonants to the rubber before vulcanization treatment.

7. Case studies

7.1 Case 1: stress corrosion cracking failure of a transmission oil product pipeline

In April 2004, an oil transportation pipeline in north part of Iran failed and caused oil leaking. Visual inspections revealed macrocracks and shallow pits on the external surface of the corroded area (**Figure 7**). Optical observation

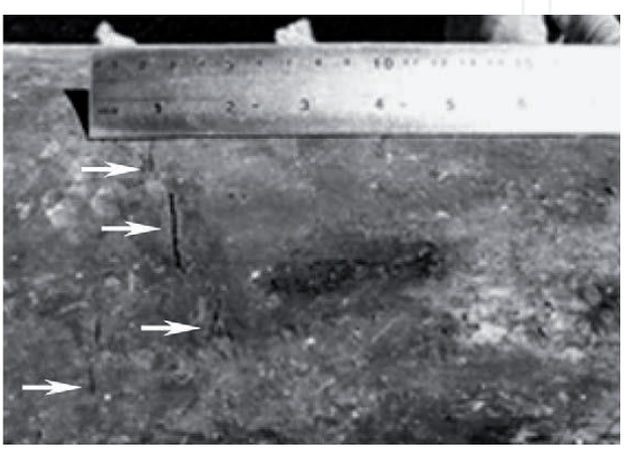

Figure 7.
Macroscopic observation of the cracking area.

indicated that cracks were started from the bottom of the pits and extended into the wall thickness as shown in **Figure 8**. There was a main singular crack and some branched cracks at the end. The crack features are characteristics of a stress corrosion cracking [60].

7.1.1 Material, environment, and source of stress

The oil transportation pipe line is made of API 5 L X52 carbon steel that is coated by polyethylene tape coating. The utilized polyethylene coating on the external surface of the carbon steel pipe gets loose and separated in some areas. As a consequence, the surface of the underground steel pipeline was uncovered to the wet soil environment. Because of the chemical reactions and the formation of carbonate-bicarbonate solution and arise of underweight stress due to rain fall and land sliding, condition was provided for SCC. Further to SCC, sulfate reducing bacteria (SRB) activities around the pipelines have accelerated corrosion and the failure process.

7.1.2 Mechanism

Two types of SCC on the external surface of underground pipelines have been diagnosticated: classical or high-pH SCC and near neutral or low-pH SCC. In high-pH SCC case, the external cracks more often initiate and progress intergranularly, and in low-pH SCC, cracks extend transgranularly. In this case, as a result of the formation of a high pH carbonate-bicarbonate solution, the cracks have been developed intergranularly (**Figure 7**). By propagation and so increasing the crack depth, chemical composition in the crack's tip changed toward low pH, and the cracks propagated transgranularly (**Figure 7**). In a critical length of crack and the presence of inclusions such as MnS, atomic hydrogen will be formed in crack's tip and penetrates into the microstructure. Formation of hydrogen was due to application of negative cathodic potential, more than 1.2 V with respect to $Cu/CuSO_4$ reference electrode. Investigations have been shown that atomic hydrogen commonly tends to concentrate in the stress concentration points, microstructure interfaces like inclusion and matrix, microvoids, and other defects. The increase in the amount of atomic hydrogen in these sites and combination together decreased the interface cohesively strength and make atomic disbanding. These led the crack growth and fracture toward a cleavage and brittle mode.

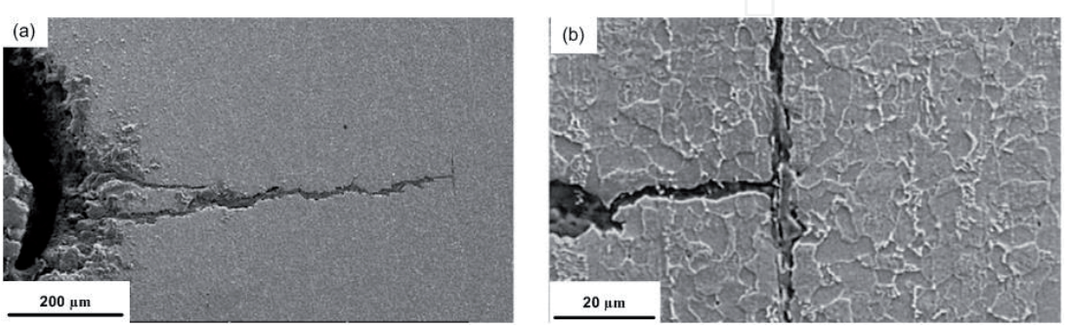

Figure 8.
(a) Initiating of cracks from pitting on the surface of the carbon steel pipe and its branched development (unetched), (b) intergranular crack growth in the microstructure (etched) [60].

7.1.3 Prevention

Utilizing a high level of negative potential (1.2 V $Cu/CuSO_4$) in cathodic protection provides condition for production of carbonate and bicarbonate which induced SCC. Therefore, controlling of the potential can be effective in reduction of these failures.

7.2 Case 2: failure of a hydroprocessing reactor

A vertical hydro-processing reactor failed only after 1 month operation. Penetrant testing (PT) revealed some cracks on the inner surface of the component. The cracks are mostly found to be initiated from the heat affected zone or HAZ of the weldments. The cracks were extended in perpendicular to the weld in the head side (**Figure 9**). Metallographic investigation showed that all the cracks had propagated essentially in transgranular mode, and they had the appearance of branching as it is shown in **Figure 10**. These features indicate occurrence of the stress corrosion cracking on the reactor [44].

7.2.1 Material, environment, and source of stress

The reactor shell is made of AISI 316L stainless steel and operates at a pressure of 4.5 MPa. The operating temperature is 200°C. The processing environment consists of some kind of neutral organic compound and hydrogen. The base metal and corrosion products were analyzed by scanning electron microscope (SEM) and energy dispersive X-ray (EDAX) analyzer. The results indicated that the reactor was made of AISI316L stainless steel. The analysis also revealed the presence of chlorides in corrosion products. The equipment history showed that the reactor was not annealed after weld though the thickness of the reactor was 45 mm. Therefore, remaining residual stress in services arise to a level of ultimate strength.

7.2.2 Mechanism

The reactor has a thickness of 45 mm. Welding was used in manufacturing processes. A high magnitude of the welding residual stress is created (in

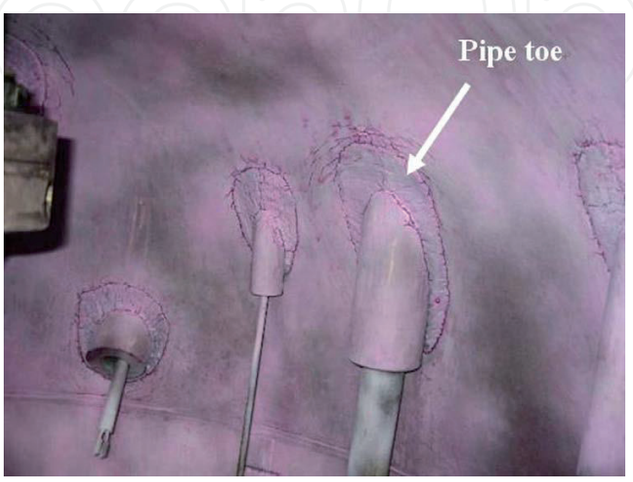

Figure 9.
Cracks in heat affected zone of the weld toe.

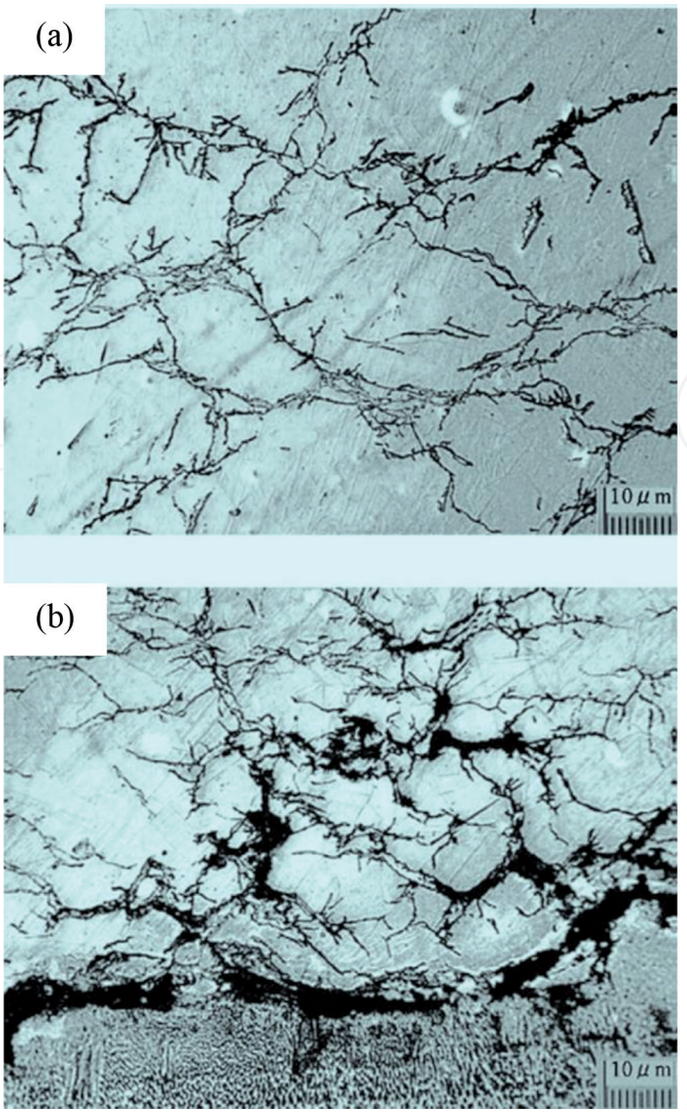

Figure 10.
The stress corrosion cracking: (a) heat affected zone and (b) the weld line.

magnitude of the ultimate strength) during welding operation. The chloride ions came from the catalysts. For the utilized catalyst, the chloride concentration is over 60 ppm. The operating temperature of the equipment is 200°C. Investigations have shown a chloride concentration of 10 ppm is enough to motive SCC in an austenitic stainless steel grade if the metal temperature is over 60°C [2]. Therefore, chloride SCC is responsible for the failure of the reactor.

7.2.3 Prevention

- The main cause of failures is the presence of high concentration of chlorides. Therefore, decreasing the concentration of this aggressive agent in the catalyst can be an effective approach. Experience on the other reactor used in the same operational conditions shows that the concentration of chloride in the catalyst should be less than 60 ppm for the AISI 316L material.

- Selecting more resistant materials to SCC. Since AISI 316L cannot tolerate such a high concentration of chloride, more corrosion-resistant alloys, such as duplex stainless steel, should be utilized if the concentration of the chloride in the catalyst cannot decrease to a proper level.

- Decreasing the magnitude of stress. As welding residual stress is a main source of stress attributed to the stress corrosion cracking, decreasing its order should decline the possibility of SCC. It means that the reactor should be stress relived after welding.

7.3 Case 3: stress corrosion cracking of a copper refrigerant tubing

Copper alloy C12200 tubes of a refrigerant failed in bend area (**Figure 11**). Failures were occurred only after approximately 6 months of services. The cracked area is shown in **Figure 12**. SEM image of fractured areas revealed the branch cracked through the microstructure, **Figure 13**, which is characteristic of a stress corrosion cracking phenomenon [61].

7.3.1 Material, environment, and source of stress

Chemical analysis of the tube materials proved the C12200 copper alloy composition. Analysis of the black foam insulation utilized with the subject copper tubing revealed the presence of ammonia by reason of the fabrication process. The stress comes from the cold-working of copper tubes during manufacturing processes.

7.3.2 Mechanism

The phosphorized copper alloy tube failed due to SCC induced by a moist ammonia environment related the black foam insulation. Although the resistance of copper alloy under dry ammonia environment is notable, gathering of moisture ease by the bent tube geometry provokes the tubing to be exposed to wet ammonia, which is substantially more. The sensitivity of the copper tubing to SCC was

Figure 11.
New and old design of refrigerating system.

Figure 12.
Macroscopic image cracked copper tube.

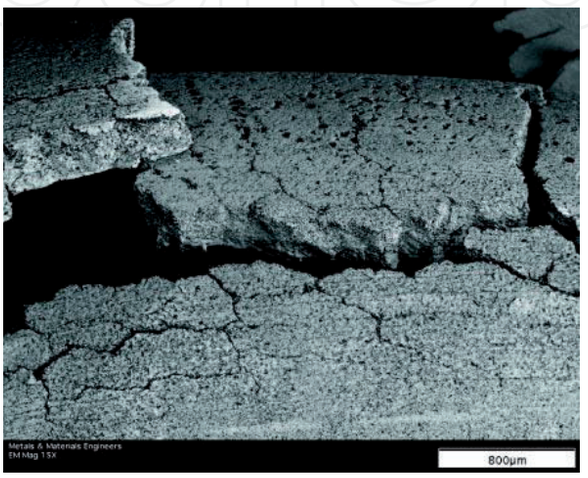

Figure 13.
SEM image of the intergranular crack growth in the copper tube.

enhanced in consequence of the cold work operation for bending the tube at an angle of 180°. Stress cycling and/or repeated loading increased the sensitivity to ammonia stress corrosion cracking as a result of the service-induced oscillational loading from the other components linked to the tube.

7.3.3 Prevention

Cold work operation generated high magnitude of residual stress which is responsible for the tube failure. Hence, it is suggested that the copper tubing be annealed after the bending operation in order to eliminate the adverse impacts of the cold working and also decrease the residual stresses available for ammonia stress corrosion cracking. Another recommendation is to avoid the installation of the tube under stress condition.

8. Conclusion

Stress corrosion cracking failure is because of combined interaction of sensitizes material, tensile mechanical stress, and corrosive environment. Chloride stress corrosion cracking of austenitic steels and seasonal cracking of copper alloys are classical example of SCC. During stress corrosion cracking, the metal or alloy is basically uncorroded over most of its surface, while fine and branch cracks growth into the bulk of material and lead the components to unpredictable premature failures. The main source of stress attributed to the stress corrosion cracking is come from the residual stress. The well-known sources of the residual stress are welding and

fabrication processes such as machining and bending. The stress must be in tensile form, and comprehensive stresses can be utilized to restrict SCC. Surface defects that either preexist or are created during service due to corrosion, wear, or other processes accelerate the stress corrosion cracking phenomenon. Therefore, the role of imperfections must be taken into account. Fracture mechanics introduced a parameter named fracture toughness or $K_{Ic} = \sigma\sqrt{\pi a}$ that considered the performance of flaws in fracture behavior of materials. According to this relation, there is a critical length of crack, α, in which the materials indicate the brittle failure. The fracture toughness in the presence of corrosive environment declines considerably and displayed by $K_{Iscc.}$ It means in conditions prone to SCC, a smaller flaw size led the materials to catastrophic brittle fractures.

If one of three SCC elements does not exist, this kind of failure will not develop. Accordingly, the solving methods can be one or more of these factors:

- Lowering the stress levels
- Eliminating aggressive species in the environment
- Changing the material is one possible
- Applying cathodic protection
- Coating that is sometimes effective
- Shot-peening that produces residual compressive stress

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